

SOLID STATE**Space Lattice**

The regular three-dimensional arrangement of atoms or ions in a crystal is usually described in terms of a space lattice and a unit cell. To see what these two terms mean, let us first consider the two-dimensional patterns shown in Figure 1. We can think of each of these three structures as a large number of repetitions in two directions of the parallel-sided figure shown immediately below each pattern.

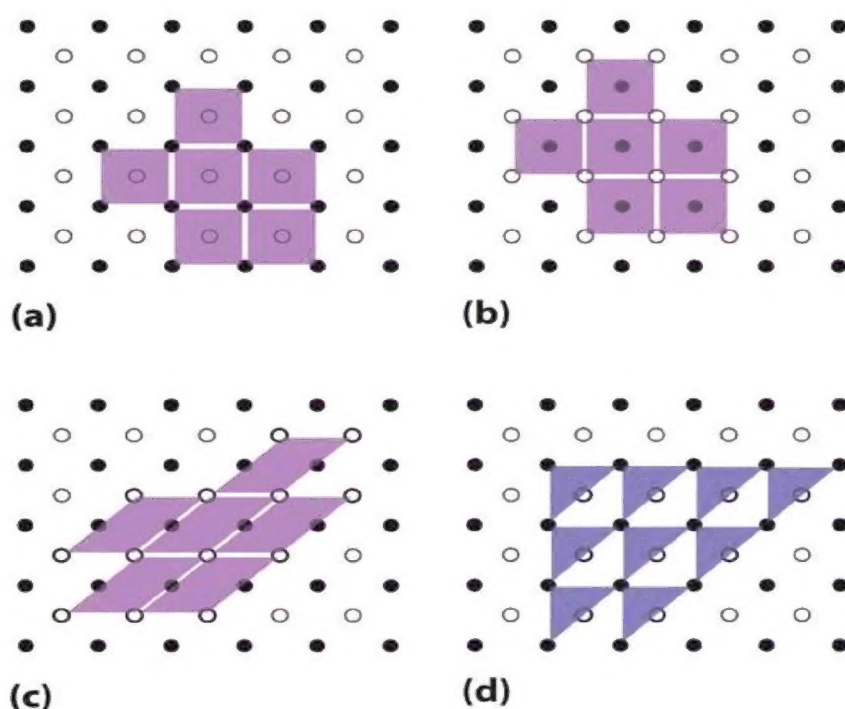


Fig. 1: Unit Cells in Two Dimensions. (a-c) Three two-dimensional lattices illustrate the possible choices of the unit cell. The unit cells differ in their relative locations or orientations within the lattice, but they are all valid choices because repeating them in any direction fills the overall pattern of dots. (d) The triangle is not a valid unit cell because repeating it in space fills only half of the space in the pattern.

This parallel-sided figure is the **unit cell**. It represents the simplest, smallest shape from which the overall structure can be constructed. The pattern of points made by the corners of the unit cells when they are packed together is called the space lattice (Figure 2). The lines joining the points of the space lattice are shown in color. Without some experience, it is quite easy to pick the wrong unit cell for a given structure. Some incorrect choices are shown immediately below the correct choice in the figure. Note in particular that the unit cell for structure b, in which each circle is surrounded by six others at the corners of a hexagon, is not a hexagon, but a parallelogram of equal sides (a rhombus) with angles of 60 and 120°.

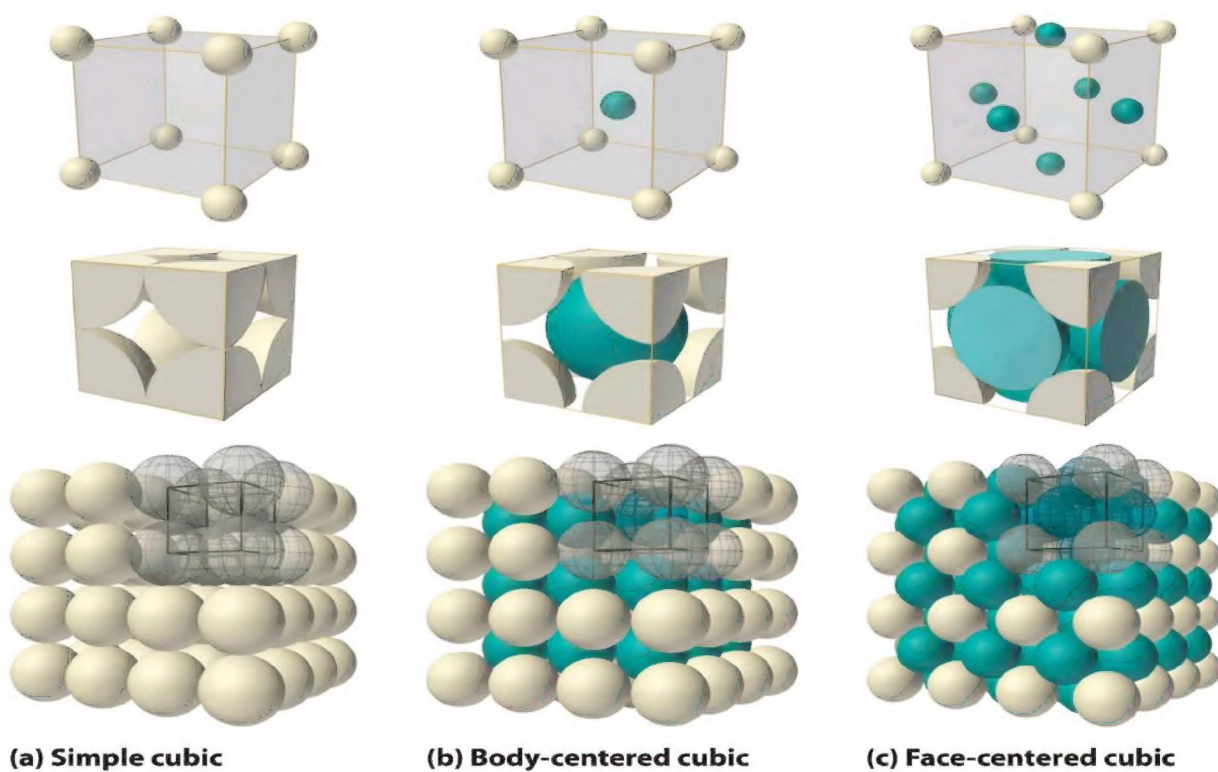


Fig. 2: The Three Kinds of Cubic Unit Cell. For the three kinds of cubic unit cells, simple cubic (a), body-centered cubic (b), and face-centered cubic (c), there are three representations for each: a ball-and-stick model, a space-filling cutaway model that shows the portion of each atom that lies within the unit cell, and an aggregate of several unit cells.

Fig. 2: illustrates the space lattice and the unit cell for a real three-dimensional crystal structure—that of sodium chloride.

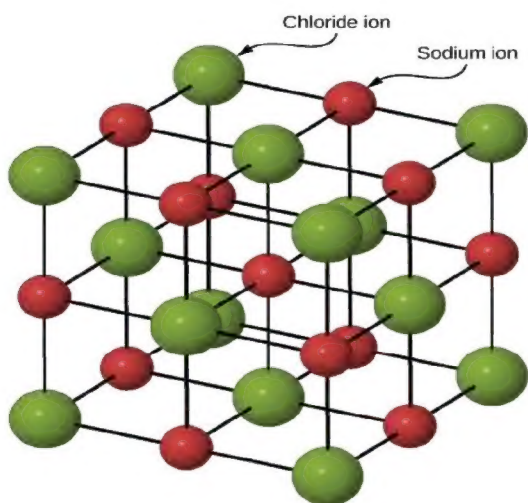


Fig. 3: (left) The crystal lattice and unit cell of a crystal of sodium chloride. Structure of the sodium chloride crystal. The sodium and chloride ions are around in a face-centered cubic (FCC) structure. Sodium ions, Na^+ , are shown in red. Chloride ions, Cl^- , are shown in green. (right) The macroscopic image on the right shows salt cubes, which demonstrate the cubic unit cell of NaCl (it doesn't always turn out this way, since crystal growth is a complex process, it's not guaranteed that the macroscopic crystal structure matches the unit cell).

This is the same structure that was shown for lithium hydride, except that the sizes of the ions are different. A unit cell for this structure is a cube whose comers are all occupied by sodium ions. Alternatively, the unit cell could be chosen with chloride ions at the comers.

The unit cell of sodium chloride contains four sodium ions and four chloride ions. In arriving at such an answer, we must bear in mind that many of the ions are shared by several adjacent cells (part c of Figure 2 shows this well). Specifically, the sodium ions at the centers of the square faces of the cell are shared by two cells, so that only half of each lies within the unit cell. Since there are six faces to a cube, this makes a total of three sodium ions. In the middle of each edge of the unit cell is a chloride ion which is shared by four adjacent cells and so counts one-quarter. Since there are twelve edges, this makes three chloride ions. At each comer of the cube, a sodium ion is shared by eight other cells. Since there are eight comers, this totals to one more sodium ion. Finally, there is a chloride ion in the body of the cube unshared by any other cell. The grand total is thus four sodium and four chloride ions.

A general formula can be derived from the arguments just presented for counting N , the number of atoms or ions in a unit cell. It is

$$N = N_{body} + \frac{N_{face}}{2} + \frac{N_{edge}}{4} + \frac{N_{corner}}{8}$$

Unit Cell

Unit Cell is the smallest part (portion) of a crystal lattice. It is the simplest repeating unit in a crystal structure. The entire lattice is generated by the repetition of the unit cell in different directions.

OR

The **structural motif** (i.e., the atom or molecule) which makes up a crystalline solid may adopt any one of a large range of distinct orderly structures. It is precisely because crystalline materials are ordered infinite three-dimensional arrays that their study is possible, since the problem may be reduced to the properties of a small portion of the array. Since the crystal contains a repeated structure, it is possible to locate a basic unit within the array which contains all the symmetry properties of the whole assembly. This basic building block is referred to as the **unit cell**.

Unit cells for most of the crystals are parallelepipeds or cubes having three sets of parallel faces. A unit cell is the basic structural unit or building block of the crystal. A unit cell is defined as the smallest parallelepiped volume in the crystal, which on repetition along the crystallographic axes give the actual crystal structure or the smallest geometric figure, which on repetition in three-dimensional space, gives the actual crystal structure is called a unit cell. The choice of a unit cell is not unique but it can be constructed in a number of ways; Fig. 1. shows different ways of representing unit cells in a two-dimensional lattice. A unit cell can be represented as ABCD or A'B'C'D' or A''B''C''D'', etc.

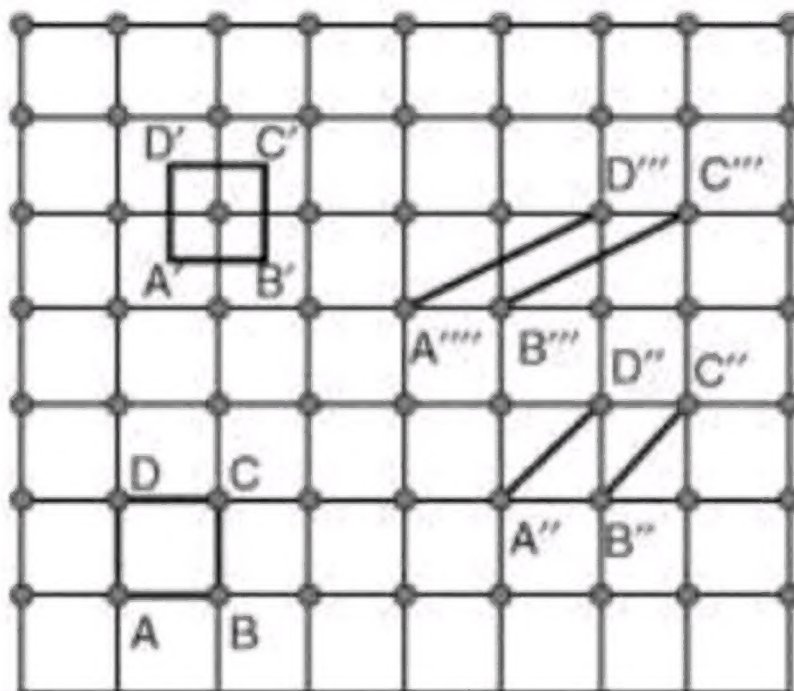
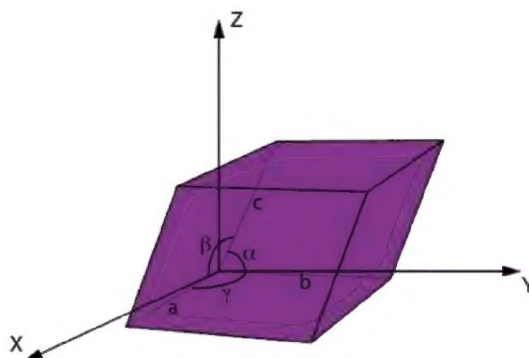


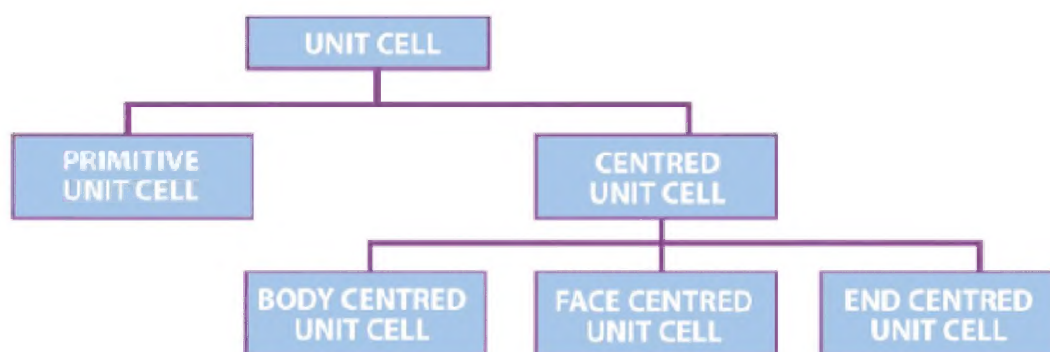
Fig. 4

1. Parameters of a Unit Cell

There are six parameters of a unit cell. These are the 3 edges which are a , b , c and the angles between the edges which are α , β , γ . The edges of a unit cell may be or may not be perpendicular to each other.



2. Types of Unit Cell



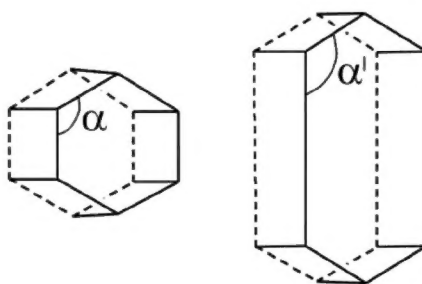
1. **Primitive Unit Cells:** When the constituent particles occupy only the corner positions, it is known as Primitive Unit Cells.
2. **Centered Unit Cells:** When the constituent particles occupy other positions in addition to those at corners, it is known as Centered Unit Cell. There are 3 types of Centered Unit Cells:
 - a. **Body Centered:** When the constituent particle at the center of the body, it is known as Body Centered Unit cell.
 - b. **Face Centered:** When the constituent particle present at the center of each face, it is known as Face Centered Unit cell.
 - c. **End Centered:** When the constituent particle present at the center of two opposite faces, it is known as an End Centered Unit cell.

Law of crystallography:

The geometry and properties of crystals and hence crystalline substances follow some fundamental laws. These laws are called laws of crystallography. There are following three laws of crystallography:

Law of constancy of interfacial angle:

The angle between any two adjacent faces is called interfacial angle. After performing a series of experiment Steno in 1669 gave a law of constancy of interfacial angle or sometimes Steno's law of constancy of angle. The law is stated as: "The angle between two adjacent planes (i.e., interfacial angle) of various crystals of same substances is always constant under same pressure and temperature" The interfacial angle is independent from the conditions of formation. External shape of the crystals may be different but interfacial angles are always same.

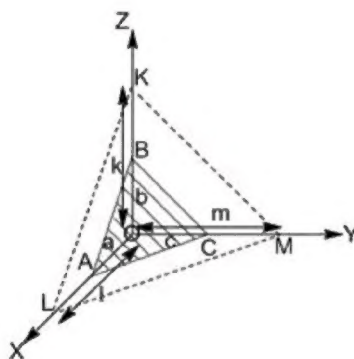


Where, $\alpha = \alpha'$

Thus, to measure the interfacial in crystal is very important in the study of crystal i.e., in crystallography.

Law of rationality of indices:

The law was given by French mineralogist R. J. Haüy in 1801 from the observation of the stacking laws required to build the natural faces of crystals. This law is stated as: The intercepts of planes of a crystal is either equal to or integral multiple of the unit intercepts along a crystallographic axis. Suppose OX, OY and OZ are the three crystallographic axes and ABC be a unit or standard plane having intercepts a, b and c respectively.



According to law of rational indices the intercepts of a face KLM on the same three axes will be simple integral multiple of a, b and c respectively. Thus;

$$OA = a = l. a$$

$$OB = b = k. b$$

$$OC = c = m. c$$

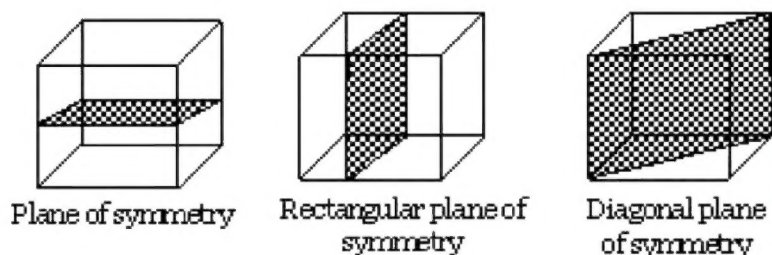
Law of constancy of symmetry:

According to this law, all crystals of a substance have the same elements of symmetry is plane of symmetry, axis of symmetry and center of symmetry.

Symmetry in Crystal: A crystal possess following three types of symmetry,

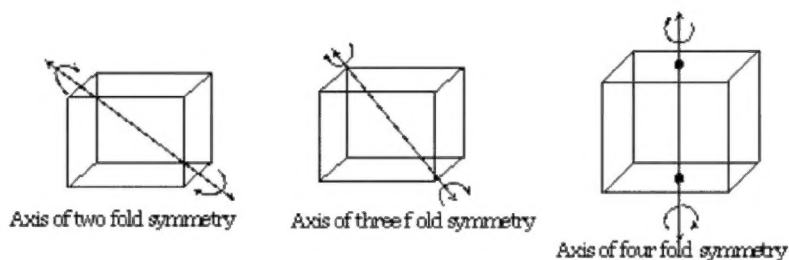
(i) Plane of symmetry:

It is an imaginary plane which passes through the center of a crystal can divides it into two equal portions which are exactly the mirror images of each other.



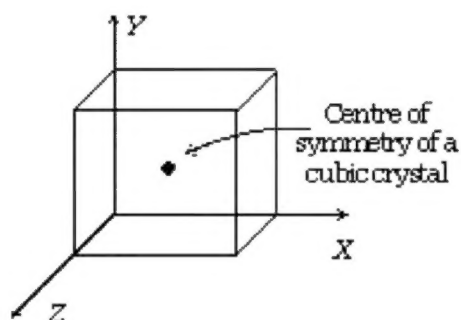
(ii) Axis of symmetry:

An axis of symmetry or axis of rotation is an imaginary line, passing through the crystal such that when the crystal is rotated about this line, it presents the same appearance more than once in one complete revolution i.e., in a rotation through 360° . Suppose, the same appearance of crystal is repeated, on rotating it through an angle of $360^\circ/n$, around an imaginary axis, is called an n-fold axis where, n is known as the order of axis. By order is meant the value of n in so that rotation through gives an equivalent configuration.



(iii) Centre of symmetry:

It is an imaginary point in the crystal that any line drawn through it intersects the surface of the crystal at equal distance on either side.



Only simple cubic system has one center of symmetry. Other system does not have center of symmetry.

The total number of planes, axes and center of symmetries possessed by a crystal is termed as elements of symmetry.

A cubic crystal possesses total 23 elements of symmetry.

Plane of symmetry $(3 + 6) = 9$

Axes of symmetry $(3 + 4 + 6) = 13$

Centre of symmetry $(1) = 1$

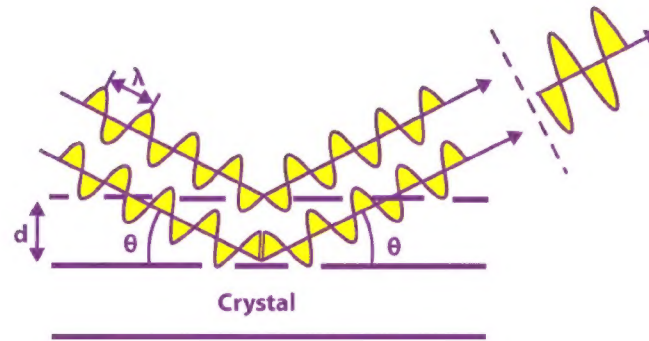
Total symmetry = 23

Bragg Equation: According to Bragg Equation:

$$n\lambda = 2d \sin\theta$$

Therefore, according to the derivation of Bragg's Law:

- The equation explains why the faces of crystals reflect X-ray beams at particular angles of incidence (θ, λ) .
- The variable d indicates the distance between the atomic layers, and the variable λ specifies the wavelength of the incident X-ray beam.
- n as an integer.

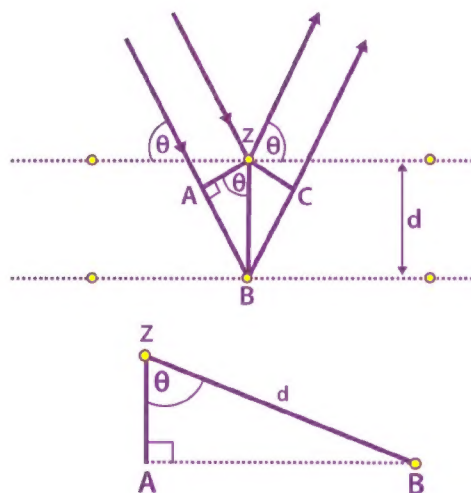


This observation illustrates the X-ray wave interface, called X-ray diffraction (XRD) and proof for the atomic structure of crystals.

Bragg was also awarded the Nobel Prize in Physics for identifying crystal structures starting with NaCl, ZnS, and diamond. In addition, to understand the structure of every state of matter by any beam, e.g., ions, protons, electrons, neutrons, with a wavelength similar to the length between the molecular structures, diffraction was developed.

Derivation of Bragg's Law

Consider the following figure of beams in which the phases of the beams coincide when the incident angle is equal to the reflecting angle. The incident beams are parallel to each other until they reach point z. When they are at point z, they strike the surface and travel upwards. At point B, the second beam scatters. $AB + BC$ is the distance travelled by the second beam. The extra distance is known as the integral multiple of the wavelength.



$$n\lambda = AB + BC$$

We also know that $AB = BC$

$$n\lambda = 2AB \text{ (equation 1)}$$

d is the hypotenuse of the right triangle ABz . Ab is the opposite of the angle θ .

$$AB = d \sin\theta \text{ (equation 2)}$$

Substituting equation 2 in equation 1

$$n\lambda = 2d \sin\theta$$

The above equation is Bragg's law expression.

Applications of Bragg's Law

There are numerous applications of Bragg's law in the field of science. Some common applications are given in the points below.

- In the case of XRF (X-ray fluorescence spectroscopy) or WDS (Wavelength Dispersive Spectrometry), crystals of known d -spacings are used as analyzing crystals in the spectrometer.
- In XRD (X-ray diffraction) the inter-planar spacing or d -spacing of a crystal is used for characterization and identification purposes.

Bragg's Diffraction

Bragg's diffraction was first proposed by William Henry Bragg and William Lawrence Bragg, in 1913. Bragg's diffraction occurs when a subatomic particle or electromagnetic radiation, waves have wavelengths that are comparable to atomic spacing in a crystal lattice.

Bragg's law Conclusion:

The concluding ideas from Bragg's law are:

- The diffraction has three parameters i.e., the wavelength of X rays, λ
- The crystal orientation defined by the angle θ
- The spacing of the crystal planes, d .

The diffraction can be conspired to occur for a given wavelength and set of planes. For instance, changing the orientation continuously, i.e., changing theta until Bragg's Law is satisfied.

Determination of Crystal structure of NaCl, KCl and CsCl

We know that KCl has a structure similar to that of NaCl. Potassium chloride is an ionic compound having a bond between an alkali metal (K) and a halogen (Cl). The ratio between the cation and anion is 1:1. There are 4 atoms in each unit cell and it belongs to a cubic crystal system.

Most of the alkali metal halides have a structure similar to that of NaCl i.e., rock salt crystal structure.

This structure is likely to be formed if the cation is smaller than the anion (a cation/anion radius ratio of 0.414 to 0.732)

The cations and anions form a separate face-centered cubic lattice, with the two lattices interpenetrating to form a 3D checkerboard pattern.

Each cation (K^+) is coordinated to 6 Cl^- anions at the vertices of an octahedron and similarly each Cl^- anion is coordinated to 6 cations at the vertices of an octahedron. Hence, the coordination number is 6.

The unit cell of KCl consists of K^+ and Cl^- ions. It has a face-centered cubic close-packed structure.

Cl^- ions having the larger size occupies the face-centers and corners of the unit cell while K^+ occupies the octahedral voids

The total number of chloride ions per unit cell

= sum of chloride ions at the face centers and corners =

$$(6 \times \frac{1}{2}) + (8 \times \frac{1}{8}) = 4 \text{ chloride ions}$$

The total number of potassium ions per unit cell

= sum of potassium ions at the 12 edge

– centers and one in the center of the cube =

$$(12 \times \frac{1}{4}) + 1 = 4 \text{ potassium ions}$$

Each ion in this lattice has six of the other kind of ion as its nearest neighbors, and twelve of the same kind of ions as its second nearest neighbors. The structure of KCl is shown below:

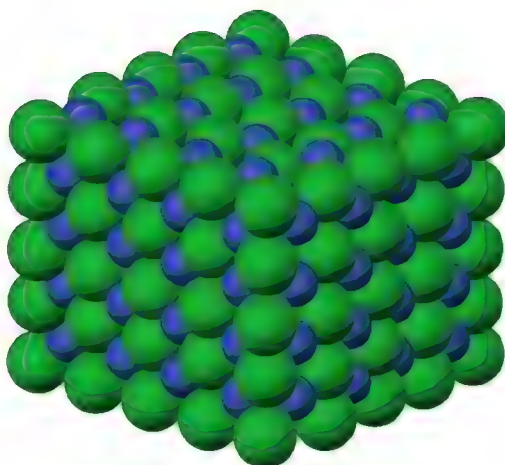


Fig. The green spheres represent the chloride ions while the grey spheres represent the potassium ions in the figure.

Note: All alkali metal chlorides except CsCl have rock salt crystal structure. It has Cs ions at the body center and chloride ions at the corners.

The position of the octahedral voids in a face-centered cubic unit cell is at the edge centers and at the body center. Hence, the potassium atoms are said to occupy the edge centers and body center in this structure.

NaCl Crystal Structure: NaCl has a cubic unit cell. It is the best thought of as a face centered cubic array of anions with an interpenetrating FCC cation lattice.

The cell looks the same whether you start with anions or cations on the corners. Each ions have a 6 coordinate and has a local octahedral geometry.

CsCl Crystal Structure: CsCl has a basic cubic structure that consists of an infinite chain of ions. The Cs (or Cl) ions sit at the eight corners of the cube. And the Cl (or Cs) sit at the center of the cube (thus it is not a body centered lattice that requires the same ion to occupy the edges and center).

Point Defects

Point defects explain about the **imperfections of solids** along with the types of point defects. Crystalline solids are formed by joining many small crystals. Different types of defects are found in crystals after the process of crystallization.

Point defects are accounted for when the crystallization process occurs at a very fast rate. These defects mainly happen due to deviation in the arrangement of constituting particles. In a crystalline solid, when the ideal arrangement of solids is distorted around a point/ atom it is called a point defect.

Defects or Imperfections in crystalline solid can be divided into four groups namely ***line defects, point defects, volume defects and surface defects***. Historically, crystal point defects were first regarded in ionic crystals, not in metal crystals that were much simpler.

There are 3 types of point defects:

1. **Stoichiometric defect**
2. **Frenkel defect**
3. **Schottky defect**

1. Stoichiometric Defect:

In this kind of point defect, the ratio of positive and negative ions (Stoichiometric) and electrical neutrality of a solid is not disturbed. Sometimes it is also known as intrinsic or thermodynamic defects.

Fundamentally, they are of two types:

- **Vacancy defect:** When an atom is not present at their lattice sites, then that lattice site is vacant and it creates a vacancy defect. Due to this, the density of a substance decreases.
- **Interstitial defect:** It is a defect in which an atom or molecule occupies the intermolecular spaces in crystals. In this defect, the density of the substance increases.

A non-ionic compound mainly shows vacancy and interstitial defects. An ionic compound shows the same in Frenkel and Schottky defect.

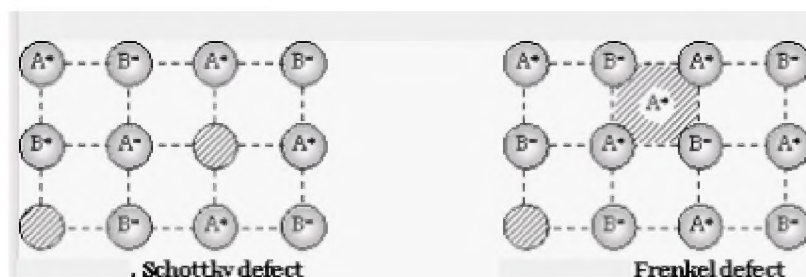
2. Frenkel Defect:

In ionic solids generally, the smaller ion (cation) moves out of its place and occupies an intermolecular space. In this case, a vacancy defect is created on its original position and the interstitial defect is experienced at its new position.

- It is also known as dislocation defect.
- The density of a substance remains unchanged.
- It happens when there is a huge difference in the size of anions and cations.
- **Example:** ZnS and AgCl.

3. Schottky Defect

- This kind of vacancy defects is found in Ionic Solids. But in ionic compounds, we need to balance the electrical neutrality of the compound so an equal number of anions and cations will be missing from the compound.
- It reduces the density of the substance.
- In this, the size of cations and anions are of almost the same.



Consequences of Schottky and Frenkel defects

1. The closeness of similar charges brought about by Frenkel defect tends to increase the dielectric constant of crystals.
2. The crystal is able to conduct electricity to a small extent by ionic mechanism. As electricity is applied a nearby ion moves from lattice site to occupy a hole which creates a new hole and another ion ready to move into it and so on.
3. The presence of holes lowers the density of the crystal.
4. The presence of holes also lowers the lattice energy or stability of the crystal. The presence of too many holes may cause a partial collapse of the lattice.

Non-Stoichiometric Defect: In this defect, the cations and anions ratio is disturbed either because of adding or removing of ions.

Types of Non-Stoichiometric Defect:

1. **Metal deficiency defect:** In this case a negative ion may be missing from its lattice site leaving a hole which is occupied by an extra electron to maintain the electrical balance. This is an excess of positive (metal) ions, although the crystal as a whole is neutral.

This defect is similar to Schottky defect but differs in having only one hole and not a pair as in the latter case. This type of defect is not very common. It has been observed in those crystals which are likely to form Schottky defect. E.g. when NaCl is treated with Na vapours, a yellow non-stoichiometric form of NaCl is obtained in which there is excess of Na⁺ ions.

An extra positive ion occupies an interstitial position in the lattice and to maintain electrical neutrality, an electron finds a place in the interstitial space.

This type of metal excess defect is somewhat similar to Frenkel defect but differs in having no holes and in having interstitial electrons. This type of metal excess defect is more common than first type of metal excess defect.

Consequences of metal excess defects

1. The crystal associated with metal excess defects of the first kind or second kind contains free electrons. Since these electrons can migrate in an electric field, such crystals can conduct electricity. However, since the number of defects and therefore the number of electrons is very small, these crystals can conduct only small amounts of current and thus termed as semi-conductors. Since, current, howsoever small, is carried by electrons is termed as n-type semiconductors.
2. The crystals with metal excess defects are generally coloured. This again is due to the free electrons. These electrons get excited easily to higher energy levels by absorption of certain wave lengths from the visible chloride is yellow, non-stoichiometric potassium chloride is lilac in colour.

2. **Metal excess defect:** There are two types of metal excess defect:

There are two possible ways in which metal excess defects can occur-

1. In the first way, one of the positive ions may be missing from its lattice. The extra negative charge may be balanced by some nearby metal ion by acquiring positive charge. It is found in compounds of transition metals. Crystals of ferrous oxide, FeO, ferrous sulphide, FeS and NiO show this type of defect.
2. In the second case, an extra negative ion may occupy an interstitial position. The extra negative charge is balanced again by means of an extra charge on one of the adjacent metal ions. The metal in this case also, should be capable of exhibiting variable valency. It should be one of large and it is not expected that they would be able to fit into the interstitial position.

Consequences of metal deficiency defects

The crystals with metal deficiency defects can also be semi-conductors. This property arises from the movement of an electron from one ion to another. In this way, the ion A^+ say to A^{++} . Thus the movement of an electron from A^+ ion is an apparent movement of A^{++} ion. This is called movement of positive hole and the substance permitting type of movement are known as p-type semi-conductors.

Colour Centres

It has been observed that if a crystal of NaCl is heated in sodium vapour. It acquires a yellow colour. This yellow colour is due to the formation of a non-stoichiometric compound of NaCl in which there is a slight excess of Na ions. What happens in this case is that some sodium

metal gets doped into the NaCl crystal each atom of which gets ionised into Na^+ and e^- due to crystal energy.

There is evidently an excess of Na^+ ions through the crystal as a whole is neutral. A little reflection would show that there are six Na^+ sites adjacent to the vacant site occupied by the electron. The extra electron is thus shared between all the six Na^+ ions which imply that this electron is not localised at the vacant Cl^- site. On the other hand, this electron is similar to the delocalised electron makes an easy transition from its ground state to an excited state. As a result, the non-stoichiometric form of NaCl appears coloured. Because of this, the sites occupied by the extra electrons are known as colour centre. These are also called F-centres. This name comes from German word Farbe meaning colour.

Law of symmetry

Besides the interfacial angles, another important property of crystals is their symmetry. The law of symmetry states that:

All crystals of the same substance possess the same elements of symmetry.

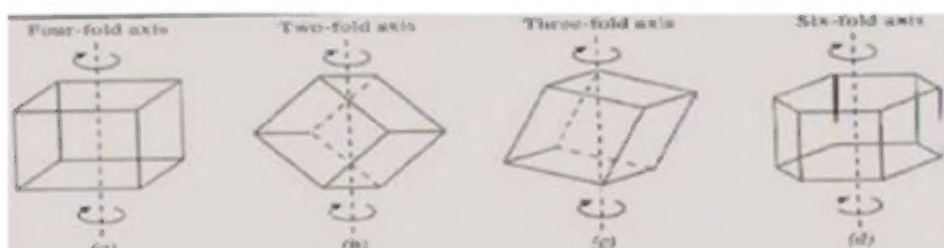
Symmetry in crystals may be with respect to a plane, a line or a point, accordingly there are three types of symmetry associated with a crystal.

Plane of symmetry

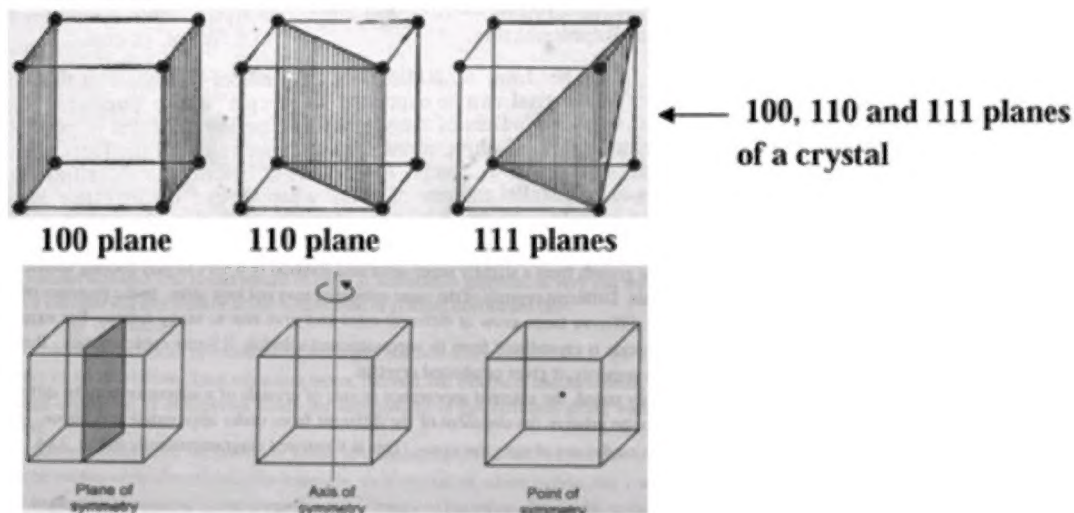
When an imaginary plane can divide a crystal into two parts such that one is the exact mirror image of the other, the crystal is said to have a plane of symmetry.

Axis of symmetry

An axis of symmetry is a line about which the crystal is rotated such that it presents the similar appearance more than once during complete rotation i.e. rotation through an angle of 360° . Depending upon its nature, a crystal may have 2-fold, 3-fold, 4-fold or 6-fold axes of rotation.



rotation of 90° each and the same appearance after the fourth rotation, such an axis is called a four-fold or tetrad axis (fig 5.6(a)). If the same similar appearance is repeated after an angle of 180° , the axis is called two-fold or diad axis (fig 5.6(b)). In the same way, if the same or similar appearance is repeated after an angle of 120° , the axis is called a three-fold or triad axis (fig 5.6(c)). If the same or similar axis is repeated after an angle of 60° , as in the case of a hexagonal crystal, the axis is called six-fold or hexad axis (fig 5.6(d)). In general, if the same or similar appearance of a crystal is repeated on rotation through an angle of $360/n$, around an imaginary axis, the axis is called an n-fold axis.



Centre of Symmetry

It is a point at the centre of the crystal so that any line drawn through it will meet the surface of the crystal at equal distance on either side.

It may be pointed out that a crystal may have number of planes or axis of symmetry but it has only one centre of symmetry.

SYMMETRY ELEMENTS OF A CRYSTAL

Any crystal or any molecule of the crystal will have some combinations of symmetry elements. These combinations of symmetry elements are known as point groups. These point groups are called classes or systems.

Sr No	Crystal system	Relative axial length	Angles	Examples
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl , CaCl_2 , CaF_2 , CaO
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	K_2PtCl_6 , $\text{Pb(NO}_3)_2$, NH_4Br
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	K_2SO_4 , KNO_3 , BaSO_4
4	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	CaCO_3 , NaNO_3
5	Hexagonal	$a \neq b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	AgI , HgS , SiC
6	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma \neq 90^\circ$	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, KClO_3
7	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$